Chlorine, Total

DOC316.53.01031

USEPA[1] DPD Method[2] **Method 8370**

ULR (2 to 500 µg/L as Cl_2) **Pour-Thru™ Cell**

Scope and Application: For detecting trace levels of chlorine and chloramines in clean waters relatively free of color and turbidity; USEPA accepted for reporting for drinking water analysis.

[1] USEPA accepted

[2] U.S. Patent 5,362,650

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 120 Instrument-specific information

Instrument	Pour-thru Kit	Cell orientation	Adapter
DR 6000	LQV175.99.20002	Arrow faces right	—
DR 5000	LZV479	—	—
DR 3900	LQV157.99.10002	Align cell flow arrows with arrows on cell compartment	—
DR 3800, DR 2800, DR 2700	5940400	1-inch (round) path aligned with arrow on the adapter	LZV585 (B)

Before starting the test:

Analyze samples immediately. Samples containing chlorine cannot be preserved for later analysis.
A reagent blank value for a combined lot of indicator/buffer reagent solutions should be determined at least once a day. If sample color or turbidity fluctuates frequently during the day, determine a reagent blank for each sample.
Ampules contain more than 1.0 mL of solution for ease of transfer. Discard excess reagent in the ampule.
Refer to the instrument User Manual for Pour-Thru cell and module assembly and installation.
Protect the Pour-Thru Cell from contamination when not in use by inverting a small beaker over the top of the glass funnel. Refer to *Treating analysis labware*.

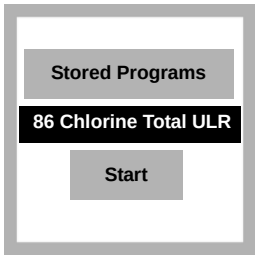
Collect the following items:

Description	Quantity
ULR Chlorine Buffer Solution, 1.5-mL ampules	1 mL
DPD Indicator Solution for ULR Chlorine, 1.5-mL ampules	1 mL
Blanking Reagent for ULR Chlorine	1 mL
Beaker, 250 mL	1
Cylinder, graduated mixing, 50-mL.	1
Pipet, TenSette®, 0.1 to 1.0 mL	1
Pipet Tips for TenSette Pipet	2

Collect the following items: (continued)

Description	Quantity
Pour-Thru Module and cell (See Instrument Specific Information)	1
Ampule Breaker	1
See *Consumables and Replacement Items* for reorder information.	

DPD method for Pour-Thru Cell



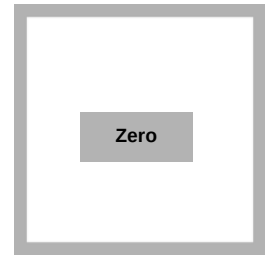
1. Select the test.

Insert an adapter if required (*Instrument-specific information*).

2. Pour at least 50 mL of sample into the Pour-Thru Cell.

3. When the flow stops, start the instrument timer.

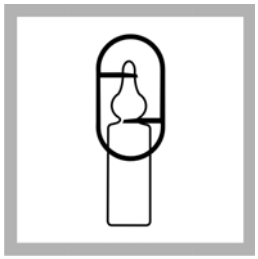
A three-minute reaction period will begin. This time allows turbidity or solids to settle and ensures a stable reading.



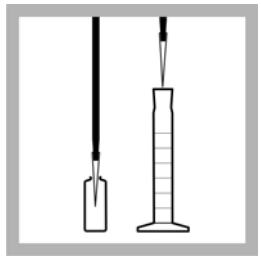
4. When the timer expires, **ZERO** the instrument.

The display will show:

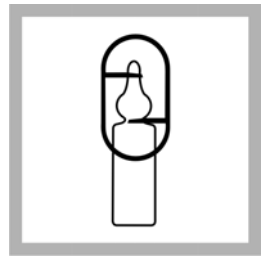
0 µg/L



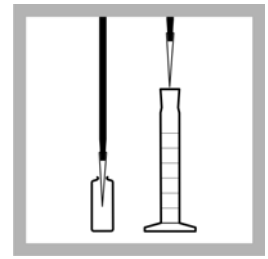
5. Open one ULR Chlorine Buffer Solution Ampule.



6. Using a TenSette® Pipet and a clean tip, transfer 1.0 mL of buffer from the ampule to a clean, treated 50-mL graduated mixing cylinder.



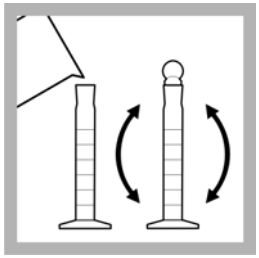
7. Open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.



8. Use a TenSette Pipet and a clean tip to transfer 1.0 mL of indicator from the ampule to the graduated mixing cylinder. Swirl to mix.

Proceed to step 9 within one minute.

DPD method for Pour-Thru Cell (continued)



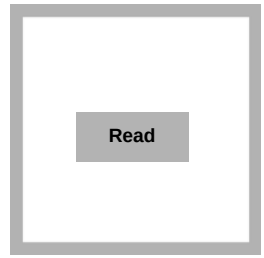
9. Prepared Sample: Avoiding extra agitation, carefully fill the cylinder to the 50-mL mark with sample. Stopper the cylinder. Gently invert it twice to mix.

10. Start the instrument timer.

A three-minute reaction time will begin.

Measure the reacted sample 3–4 minutes after mixing the sample and reagents. If less than three minutes elapses, the reaction with chloramines may be incomplete. A reading after four minutes may result in higher reagent blank values.

11. Pour the contents of the graduated mixing cylinder into the Pour-Thru cell.

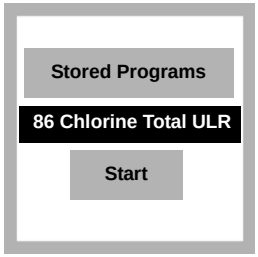


12. When the timer expires, **READ** the results in µg/L chlorine.

If a dechlorinating agent (e.g. sulfite or sulfur dioxide) is present, the sample result (corrected for the reagent blank) will read “0” or a slightly negative value.

13. Flush the Pour-Thru Cell with at least 50-mL of deionized water immediately after use.

Determining the reagent blank value



1. Select the test.

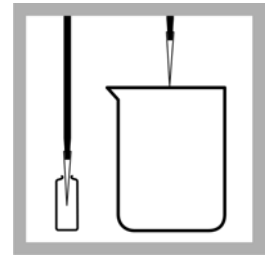
Make sure that the reagent blank setting is off.

See the user manual for information.

2. Install the Pour-Thru module.

Flush the Pour-Thru cell with 50 mL of deionized water.

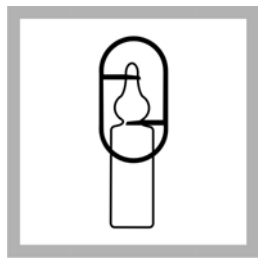
3. Collect about 100 mL of deionized or tap water in a clean, 250-mL beaker.



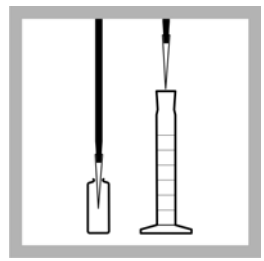
4. Use a TenSette® Pipet to add 1.0 mL of Blanking Reagent to the beaker. Swirl several times to mix.

The Blanking Reagent removes chlorine and chloramines from the water. ***Note: This solution will be used in Step 10.***

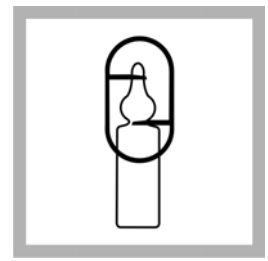
5. Access the general timer and set it for five minutes. Start the timer.



6. After the timer expires, open one ampule of ULR Chlorine Buffer Solution.

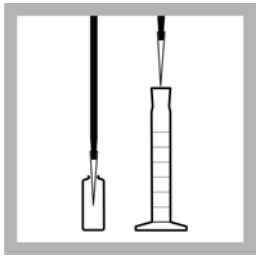


7. Use a TenSette Pipet and a clean tip to transfer 1.0 mL buffer from the ampule to a clean 50 mL mixing graduated cylinder.

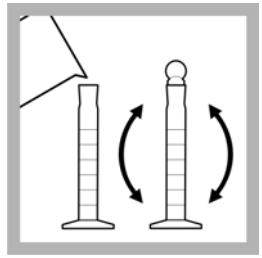


8. Open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.

Determining the reagent blank value (continued)



9. Use a TenSette Pipet and a clean tip to transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix the reagents. Proceed to step 10 within one minute.

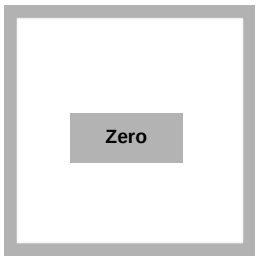


10. Fill the cylinder to the 50-mL mark with dechlorinated water from step 4. Cap and invert twice to mix. Save the remaining water for step 12.

11. Start the instrument timer.

A three-minute reaction time will begin.

12. During the reaction period, flush the Pour-Thru Cell with the remainder of original dechlorinated water from step 10.



13. When the flow stops, **ZERO** the instrument.

The display will show: 0 µg/L Cl_2.

14. When the timer expires, pour the contents of the cylinder into the Pour-Thru Cell. **READ** the results in µg/L chlorine.

15. Use this value to correct the sample result obtained in this procedure.

See the user manual for details on saving the reagent blank value.

16. Flush the Pour-Thru Cell with at least 50-mL of deionized water immediately after use.

Interferences

Table 121 Interfering substances and levels

Interfering substance	Interference levels and treatments
Bromine, Br_2	Interferes at all levels
Chlorine Dioxide, ClO_2	Interferes at all levels
Chloramines, organic	May interfere
Copper, Cu^{2+}	Greater than 1000 µg/L
Iodine, I_2	Interferes at all levels.
Iron (Fe^{3+})	Greater than 1000 µg/L

Table 121 Interfering substances and levels (continued)

<table>
<tr><th>Interfering substance</th><th>Interference levels and treatments</th></tr>
<tr><td>Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})</td><td>1. Adjust sample pH to 6–7 with 1.000 N Sulfuric Acid[1].
2. Add 9 drops Potassium Iodide (30 g/L)[1] to an 80-mL sample.
3. Mix and wait 1 minute.
4. Add 9 drops Sodium Arsenite[1, 2] (5 g/L) and mix.
5. Analyze the treated sample as described in the procedure above.
6. Subtract the result of this test from the original analysis to obtain the correct concentration.</td></tr>
<tr><td>Nitrite, NO_2^- (uncommon in clean waters)</td><td><table><tr><th>mg/L nitrite</th><th>Apparent µg/L chlorine</th></tr><tr><td>2.0 mg/L</td><td>3 µg/L</td></tr><tr><td>5.0 mg/L</td><td>5 µg/L</td></tr><tr><td>10.0 mg/L</td><td>7 µg/L</td></tr><tr><td>15.0 mg/L</td><td>16 µg/L</td></tr><tr><td>20.0 mg/L</td><td>18 µg/L</td></tr></table></td></tr>
<tr><td>Ozone</td><td>Interferes at all levels</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH or highly buffered samples</td><td>Adjust to pH 6–7</td></tr>
</table>

[1] See *Optional reagents and apparatus*.

[2] Samples treated with sodium arsenite for interferences will be hazardous waste as regulated by the Federal RCRA for arsenic (D004). Refer to the current MSDS for safe handling and disposal instructions.

Sample collection, storage and preservation

- Analyze samples for chlorine immediately after collection. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.
- Avoid plastic containers since these may have a large chlorine demand.
- Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.
- A common error in testing for chlorine is failure to obtain a representative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. Perform the chlorine analysis immediately.

Treating analysis labware

Glassware used in this test must be chlorine demand-free. Fill the 100-mL mixing cylinder and sample container with a dilute solution of chlorine bleach prepared by adding 1 mL of commercial bleach to 1 liter of water. Soak in this solution at least one hour. After soaking, rinse thoroughly with deionized water and allow to dry before use.

Treat the Pour-Thru Cell similarly with dilute bleach and let stand for several minutes. Rinse several times with deionized water.

Cleaning the Pour-Thru cell

The Pour-Thru Cell may accumulate a buildup of colored reaction products, especially if the reacted solutions are allowed to remain in the cell for long periods after measurement. Remove the buildup by rinsing the cell with 5.25 N Sulfuric Acid followed by several rinsings with deionized water.

Accuracy check

Required for accuracy check:

- Low Range Chlorine PourRite® Ampule Standard Solution, 25 to 30-mg/L (25,000 to 30,000 µg/L) Cl_2
- TenSette® Pipet and tips
- Ampule Breaker

Standard additions method (sample spike)

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select Options>More>Standard Additions from the instrument menu.
3. Default values for standard concentration, sample volume and spike volumes can be accepted or edited. Enter the chlorine concentration from the ampule package. After values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
4. Open a Low Range Chlorine Voluette Ampule Standard Solution, 25 to 30-mg/L (25,000 to 30,000 µg/L) Cl_2.
5. Prepare three sample spikes. Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to three 50-mL samples, respectively. Swirl gently to mix.
6. Analyze each sample spike as described in the procedure above, starting with the 0.1 mL sample spike. Accept each standard additions reading by pressing **READ**. Each addition should reflect approximately 100% recovery.
7. After completing the sequence, press **GRAPH** to view the best-fit line through the standard additions data points, accounting for the matrix interferences. Press **IDEAL LINE** to view the relationship between the sample spikes and the “Ideal Line” of 100% recovery.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change	
			Point of curve	Concentration
86	295 µg/L Cl_2	290–300 µg/L Cl_2	Entire range	17 µg/L Cl_2

Summary of method

This method is designed for clean water, low in color and turbidity. The main applications include monitoring for trace chlorine break-through of activated carbon beds and feedwater to reverse osmosis membranes or ion-exchange resins.

Several modifications to the normal DPD chlorine method are necessary to measure trace levels of chlorine. The Pour-Thru Cell must be used in the spectrophotometer. Liquid reagents are also required. The reproducible optics of the Pour-Thru Cell give more stable readings than is possible with movable sample cells, resulting in more stable measurements.

The reagents are packaged in ampules and sealed under argon gas to ensure stability. Use of liquid reagents eliminates any slight turbidity that might be caused by using powdered reagents. Due to the possible oxidation of the reagents (which could give a positive chlorine reading in the blank), a reagent blank must be determined at least once a day for each lot of reagent used. This reagent blank value is subtracted from the sample result and the corrected value is the actual chlorine concentration. Test results are measured at 515 nm.

Consumables and Replacement Items

Required Reagents

Description	Quantity/Test	Unit	Catalog number
ULR Chlorine Reagent Set (approximately 20 tests), includes:			2563000
ULR Chlorine Buffer Solution, 1.5-mL ampules	1 mL	20/pkg	2493120
DPD Indicator Solution for ULR Chlorine, 1.5-mL ampules	1 mL	20/pkg	2493220
Blanking Reagent for ULR Chlorine	1 mL	29 mL	2493023

Required Apparatus

Description	Quantity	Unit	Catalog number
PourRite® Ampule Breaker	1	each	2484600
Beaker, 250-mL	1	each	50046H
Cylinder, graduated mixing, 50-mL	1	each	189641
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	1970001
Pipet Tips, for TenSette Pipet 1970001	2	50/pkg	2185696

Recommended Standards

Description	Unit	Catalog number
Chlorine Standard Solution, PourRite® Ampule, 25–30 mg/L, 2-mL	20/pkg	2630020

Optional reagents and apparatus

Description	Unit	Catalog number
Potassium Iodide, 30 g/L	100 mL	34332
Sodium Arsenite, 5 g/L	100 mL	104732
Sulfuric Acid, 1 N	100 mL	127032
Sulfuric Acid, 5.25 N	1000 mL	244953
pH Paper, 0 - 14 pH range	100/pkg	2601300
Pipet Tips, for TenSette Pipet 1970001[1]	1000/pkg	2185628
Voluette Ampule breaker 10 mL	each	2196800
Chlorine Standard Solution, 2-mL PourRite® Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette® ampules, 50–75 mg/L	16/pkg	1426810

[1] other sizes are available

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